The Institute of Research

/LEHIGH UNIVERSITY

TO: Office of Grants and Research Contracts
Attention: Code SC
National Aeronautics and Space Administration
Washington, D. C. 20546

SUBJECT: Fourth Semi-annual Progress Report
on
"Investigation of the Solidification, Structure and Properties of Eutectic Alloys Including Consideration of Properties Control"

NASA Research Grant: NGR-39-007-007

SUBMITTED BY:

R. W. Hertzberg, Assistant Professor
Co-investigator

R. N. Tauber, Assistant Professor
Co-investigator

R. W. Kraft, Professor
Principal Investigator

DATE:

July 1967
(Submitted Sept. 1967)

Pages 15
Code-0

INVESTIGATION OF THE SOLIDIFICATION, STRUCTURE AND PROPERTIES OF EUTECTIC ALLOYS

INTRODUCTION:

Four graduate students have been conducting their dissertation research under the auspices of Grant NGR 39-007-007 during the reporting period covered (first half of 1967). Each of the four programs has the common feature that they were concerned with 'controlled eutectics,' that is, with highly anisotropic two phase composite materials prepared by unidirectionally solidifying binary eutectic alloys. It so happens that each of the four graduate students has also recently completed or will soon complete his dissertation research. (In fact, this report was delayed so that completed work could be reported.) The situation with respect to project titles, status of the various projects and continuing effort is summarized in Table I on the next page.

The rather high level of effort (i.e.--four graduate assistants) was possible because two of the graduate assistants did not require appreciable stipend payments and funds were therefore required for only their research expenses. The continuing work however is not at the same level of effort because the grant only provides funds for two graduate assistants.

This report consists of abstracts and brief commentaries or summaries of the four thesis programs. It is planned to prepare each in the form of a technical paper or papers; copies of the various manuscripts as submitted to various journals will be forwarded to NASA headquarters as soon as they are prepared.

This work has been done under the supervision of the three faculty investigators, all of whom have drawn a portion of their salary from the grant.

TABLE I

	Graduate Student	Project or Thesis Title	Status
1.	Cdr. R. Thomas Quinn, U.S.N.	Structure and Elevated Temperature Mechanical Behavior of Unidirectionally Solidified Ni-Ni_3Nb Eutectic Alloy	Research completed. Ph.D. degree to be awarded in Oct. 1967. Cdr. Quinn has been reassigned in the Navy.
2.	Mr. Solomon Musikant	Galvano Thermomagnetic Effects in Directionally Aligned Eutectics	Research completed. Ph.D. degree to be awarded in Oct. 1967. Mr. Musikant plans to stay at Lehigh as a post-doctoral research associate on other projects.
3.	Mr. William Hoover	Ambient Temperature Fatigue and Fracture Behavior of Aligned Al-Al_3Ni Eutectic	Master's degree research requirements met. Mr. Hoover will continue to explore the subject for his Ph.D. dissertation research.
4.	Mr. W. Gary Watson	Coarsening Behavior of Al-Al_3Ni Eutectic at Elevated Temperatures	Master's degree research requirements met. Mr. Watson has joined industry.
5.	To be assigned	- -	A master's or doctor's candidate will be assigned as soon as practical to the other vacancy on this grant. It is planned to have him work in the general area of physical properties if at all possible.

STRUCTURE AND ELEVATED TEMPERATURE MECHANICAL BEHAVIOR OF UNIDIRECTIONALLY SOLIDIFIED Ni-Ni_3Nb EUTECTIC ALLOY

Abstract

Mechanical behavior of the unidirectionally solidified eutectic Ni-Ni_3Nb has been studied from ambient temperature to 1000°C. X-ray diffraction and metallographic techniques were used to determine the crystallographic relationships between the two phases. The crystallographic studies showed the aligned alloy has the following relationship between the FCC α Ni and the orthorhombic (D_{2h}^{13}) Ni_3Nb phase:

Interfacial plane $\parallel$ (111) α Ni $\parallel$ (010) Ni_3Nb

Growth direction $\parallel$ $[1\bar{1}0]$ α Ni $\parallel$ $[100]$ Ni_3Nb

Hot hardness, hot tensile, creep-rupture, compression, and bend tests were used to investigate the mechanical properties of the eutectic alloy. The results of the mechanical tests of the controlled alloy compared to the "as-cast" alloy of the same composition prove the unidirectionally solidified Ni-Ni_3Nb eutectic alloy is strengthened in a direction parallel to the growth direction. A relationship is also shown between the softening temperatures of the intermetallic compound, the unidirectionally solidified Ni-Ni_3Nb, and the temperature at which the tensile strength of the controlled alloy begins to decrease significantly.

Examination of fractured specimens shows the alloy fails after cracks are nucleated by cleavage of the Ni_3Nb phase. These cleavage failures in the intermetallic occur parallel to retained markings in a polished surface; they are probably manifestations of twinning. The retained markings are found in all specimens fractured by tensile loading, including creep-rupture, at all the test temperatures, ambient to 1000°C. Quantitative metallographic techniques reveal that the retained markings are occurring on $\{112\}$ type planes in the inter-

metallic phase. Further, the X-ray data from the heavily marked regions show the Ni_3Nb phase has been severely deformed. The X-ray results did not give sufficiently clear orientations of the Ni_3Nb to determine an exact twinning mode.

Comments:

This program was initiated about two years ago with the objective of learning more about the behavior of eutectic composites at elevated temperatures. It was also hoped that the alloy chosen for investigation would have useful mechanical properties.

As indicated in the abstract, particularly in the last paragraph, considerable progress was made on the primary objective. A common failure mode, which is what limits the strength of the material, was found for all specimens tested in tension. The evidence obtained indicates that some type of twinning mechanism in the intermetallic reinforcing phase immediately precedes failure--an observation quite relevant to the behavior of modern high strength alloys in general since many of them are 'reinforced' with intermetallic phases. Unfortunately it was not possible to unequivocably establish the supposed twinning mode in this program because of the extensive plastic deformation which occurred.

With regards to the secondary objective it can be said the controlled Ni-Ni_3Nb eutectic has a rupture strength comparable to the Nimonic alloys but it is not as strong as some of the more recently developed alloys. One hundred hour rupture strengths of approximately 80 ksi at 600°C, 48 ksi at 750°C and 15 ksi at 900°C were observed. All specimens exhibited a remarkably stable microstructure under all test conditions, but evidences of oxidation attack were noted at the higher temperatures.

It is concluded from these results that much information of value relevant to composites in general--their deformation behavior, mechanical properties, factors governing strengthening and failure mechanisms, etc.--can be learned from a study of controlled eutectics.

GALVANO THERMOMAGNETIC EFFECTS IN DIRECTIONALLY ALIGNED EUTECTICS

Abstract:

Galvano-thermomagnetic effects have been investigated in a number of binary and pseudo binary directionally aligned eutectics. The systems studied were the Bi-Zn, Bi-Cd, InSb-Sb and InSb-MnSb. In each case the properties of the aligned eutectics were compared to those of the constituents.

Previous experimental work on the InSb aligned eutectics and the theory of the electronic behavior of such composites have been reviewed. The Bi eutectics were studied because of the current interest in bismuth based alloys for use in Nernst-Ettingshausen energy conversion.

In the case of the two bismuth eutectics the second phase solidifies in the form of plates. The second phase forms as triangular rods in the InSb-Sb eutectic while the second phase occurs as fine fibers in the InSb-MnSb alloy. Resistivity, magnetoresistivity, Seebeck coefficient, magneto Seebeck effect, Nernst-Ettingshausen coefficient, and Hall coefficient were measured for each system within the temperature range 100° to 375°K. Magnetic fields up to 11 kilogauss were employed.

Each alloy was tested in the direction along the ingot growth (longitudinal specimen) and in the direction transverse to the growth (transverse specimen). It was found that in these highly anisotropic materials the resulting properties were very sensitive to orientation. Properties were explained on the basis of the morphological details of the structures.

Simple electrical analogs of the structure were found to be capable of qualitative explanation of the resistivity and Seebeck coefficient results. Magnetic effects were correlated with the effects of the magnetic field on the mobilities of the electron and hole charge carriers. The effects of grain orientations and grain boundaries on the mobilities of the carriers were considered. Doping effects on the characteristics of the matrices were found

to be highly influential in modifying the properties of the composites.

In each case, the matrix was a semimetal or a semiconductor while the second phase exhibited highly metallic characteristics. The metallic second phase is oriented along the growth direction. Therefore, in the transverse specimens shorting effects of the metallic phase tended to short out the Nernst voltage and the Hall voltage. In the longitudinal direction the metallic plates or fibers tended to reduce the resistivity and short out the Seebeck voltage.

For example, in the Bi-Zn eutectic longitudinal specimen at 300°K, ρ_{11} for a pure bismuth specimen was found to be 1.5×10^{-4} Ω cm compared to 1.36×10^{-4} Ω cm for the composite. In the same specimens the Seebeck coefficient of the bismuth was -54μ V/°K compared to -31μ V/°K in the composite. In the transverse specimens of the same materials the change in Seebeck coefficient is much less marked $\alpha_{\perp} = -71\mu$ V/°K for bismuth compared to $\alpha_{\perp} = -61\mu$ V/°K for the Bi-Zn eutectic.

The Hall voltage for the pure bismuth longitudinal specimen was found to be 0.25 cm^3C^{-1} at 300°K whereas no Hall voltage could be measured in the Bi-Zn eutectic. At 140°K the Nernst-Ettingshausen coefficient for the pure bismuth longitudinal specimen was measured as 70μ V/°K at 11 kilogauss compared to 28μ V/°K for its eutectic counterpart.

The properties of the Bi-Cd eutectic were found to be quite metallic because of the high volume fraction of Cd (42%) in this alloy.

The properties of the InSb eutectic alloys were sensitive to the doping levels in the matrix. In both InSb alloys the matrix was determined to be p-type and the characteristics of the composites reflected the basic properties of the p-type semiconductor matrix.

The InSb-MnSb eutectic is somewhat unusual because the second phase fibers are ferromagnetic. The properties of the alloy measured in this investigation were found to be almost completely insensitive to the magnetic field.

Comments:

As mentioned in a previous progress report this program was initiated to explore a relatively new area of materials research. It was thought that highly anisotropic two phase alloys should exhibit unusual and interesting physical properties. Since there was practically no theory and very little prior experimental work upon which to base this belief the work consisted of the systematic measurement of several different electronic properties of four different alloys in both the transverse and longitudinal directions. The second phase of the work consisted in trying to make sense of the results, that is in endeavoring to 'explain' gross differences, sign changes, nil effects and so on among all the variables studied.

The analysis was remarkably successful as indicated in the abstract. As a result of this research four specific suggestions for future research programs which conceivably might lead to new materials for special applications were evolved.

AMBIENT TEMPERATURE FATIGUE AND FRACTURE STUDIES

Summary:

The first portion of this program, the graduate assistant's master's degree research activities, has been completed but not yet written. For this reason the results are presented in the form of an informal summary.

At the last reporting time, the research program on ambient temperature fatigue and fracture had just begun. At the present time, all the experimental work has been completed, the results are being interpreted, and a paper is being written.

A series of about thirty unidirectionally solidified specimens of high purity Al-Al_3Ni have been tested in tension-tension fatigue following the previously described procedure. The data from these specimens has been used to develop both a stress vs. number of cycles to failure curve and a strain to fracture vs. number of cycles to failure curve for this material over a range from 1/4 cycle to 80,000 cycles.

A macroscopic examination of these specimens indicates that the shear walls on the fracture surface become steeper as the number of cycles to failure increases (Figures 1-3). At the higher stress levels, the fatigue crack propagates by a combination of shear through the Al matrix but mostly by fiber fracture as previously reported. At lower stresses ($\Delta\sigma < 18{,}000$ psi), the fatigue crack begins to propagate parallel to the stress axis (and hence the Al_3Ni fibers) as shown by the vertical fracture walls in Figure 3. When a specimen of this type is examined metallographically, it is observed that the crack has indeed propagated parallel to the Al_3Ni fibers (Figure 4).

Fractographic analysis fails to give any evidence of broken fibers and hence confirms the metallographic analysis. Fractographically, a large amount of interfacial failure is observed at the area near the notch root (Figure 5). Further up the fracture wall, crack propagation through the Al matrix and an

absence of interfacial failure is observed (Figure 6). As discussed in the forthcoming paper, this behavior is explained through the use of crystallography considerations and additional observations.

The strain to fracture data indicates that as the stress level is decreased, the total strain to fracture increases. It is believed that this constitutes evidence that an isostrain approach to the fatigue of this type of material is not valid.

A method of producing sound specimens of this alloy with a random as-cast structure has been developed in order to compare the fracture mechanisms of the controlled and uncontrolled morphologies under cyclic loading. Specimens of the as-cast structure were tested in the same fashion as the controlled specimens. The stress vs. number of cycles curve for the as-cast structure proved inferior to the unidirectionally solidified structure in most stress ranges. Fractographic and metallographic analysis of the as-cast specimens indicate that as the stress level is lowered, the fatigue crack tends to propagate through the colony boundaries which are devoid of any Al_3Ni particles. Thus in both morphologies, under high cycle fatigue conditions, the crack avoids the Al_3Ni phase as much as possible.

In the as-cast fatigue specimens, fatigue striations are observed in the Al matrix; striations were never seen in fatigue failure of the specimens with controlled microstructures.

A STUDY OF THE ELEVATED TEMPERATURE COARSENING BEHAVIOR

OF UNIDIRECTIONALLY SOLIDIFIED Al-Al_3Ni EUTECTIC

Abstract:

The coarsening behavior of directionally solidified Al-Al_3Ni was studied by a quantitative metallographic technique. It was observed that coarsening progressed by the dissolution of some fibers and subsequent growth of others with no apparent tendency toward fiber shortening.

Measurements revealed that the driving force for coarsening was the reduction in interfacial surface area per unit volume, S_V. S_V was found to be proportional to the square root of the number of fibers per unit area measured on a surface perpendicular to the ingot growth axis. Based on the experimental observations, a model was developed which predicts S_V to be inversely proportional to the square root of heat treatment time, indicating that the rate controlling process is diffusion rather than interfacial dissolution. Activation energy determinations suggest that the diffusing species is Ni (in Al).

Comments:

This program was initiated in spite of the fact that a similar program had been done in another laboratory on the same material. The reason for this apparent duplication of effort is that the investigators of this NASA grant were (and still are) of the opinion that the previous work was not of sufficient depth to provide a true understanding of the mechanism controlling coarsening of the composite at elevated temperatures. Therefore in the present work measurements were made of fiber size and fiber size distributions on specimens heated at various temperatures close to the eutectic temperature for times up to 500 hrs. As indicated in the abstract the results show that diffusion rather than dissolution is the factor which limits microstructural stability of this composite material.

It should be pointed out that the analysis of the results is continuing. In general, the problem of separating the effects of temperature, time and initial microstructure (all three considered as independent variables) on final microstructure (the dependent variable) has never been satisfactorily solved. Since the data obtained on this project are considered to be unique attempts are being made to obtain a still more fundamental understanding by using a graphical multiple correlation technique in which no assumptions have to be made about the nature of the functional dependence of the independent variables on the dependent variable.

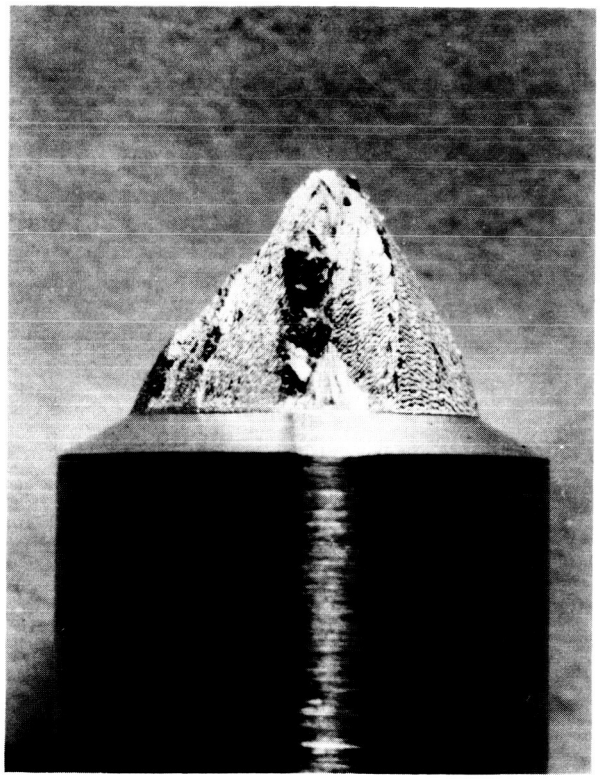

Figure 1 - Macrophotograph of a typical tensile specimen, 10X.

Figure 2 - Macrophotograph of a fatigue specimen which was cycled at $\Delta\sigma$=29,000psi for 34 cycles before fracture, 10X.

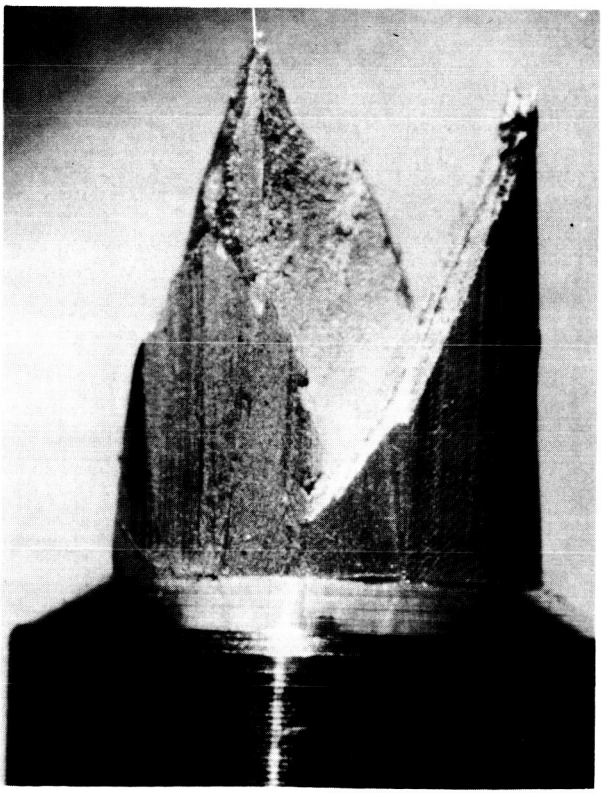

Figure 3 - Macrophotograph of a fatigue specimen cycled at $\Delta\sigma$=12,600psi for 66,417 cycles, showing crack propagation parallel to the loading axis, 12X.

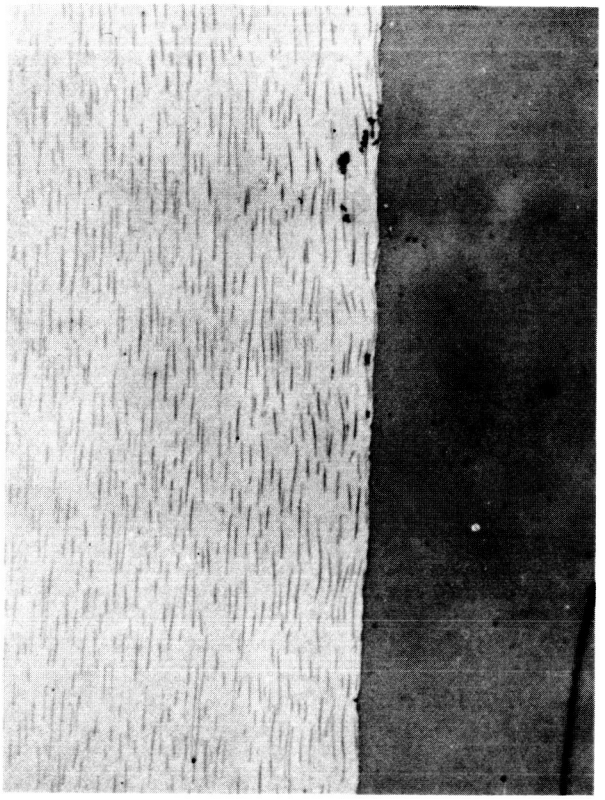

Figure 4 - Photomicrograph of the low stress fatigue crack which grew parallel to the Al_3Ni fibers, 250X.

Figure 5 - Electron micrograph showing crack propagation through the matrix in a low stress fatigue specimen, 2800X.

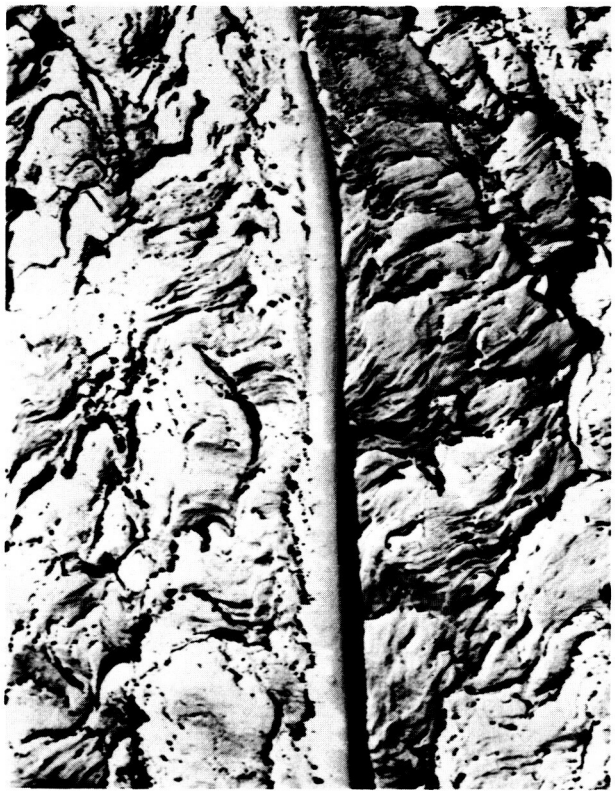

Figure 6 - Electron micrograph illustrating interfacial failure in a low stress fatigue specimen, 8200X.